

# COALIFICATION OF LIGNIN TO FORM VITRINITE: A NEW STRUCTURAL TEMPLATE BASED ON AN HELICAL STRUCTURE.

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## INTRODUCTION

The structural evolution of vitrinite has been previously studied in our group through detailed characterization of coalified wood which spans the entire coalification range (1-6). The use of coalified logs was demonstrated to be especially useful as it removes the superposed problem of maceral scale heterogeneities from the problem of identifying fundamental transformations which delineate the coal's chemical structural evolution. The net result of these detailed studies using <sup>13</sup>C NMR and pyrolysis/gas chromatography/ mass spectrometric (py/gc/ms) methods is the identification of several key chemical structural transformations which typify the coalification of woody material into high volatile bituminous coal. By comparisons of the chemical compositions of wood at various stages of coalification, one can infer specific reactions responsible for coalification.

Although, the coalification series represents a continuum of parallel and serial processes; several principle stages of coalification are clearly evident. The initial, biochemical, stage of coalification is characterized by a complete loss in hemicellulose, a significant reduction in cellulose, and selective preservation, with minimal alteration, of lignin derived material (2, 7). Early diagenetic changes accompanying the transformation from brown coal into lignite result in a near complete removal of cellulose and some modification of the lignin, a macromolecular material composed of methoxyphenols with a polyhydroxypropanol side-chain as basic building blocks. These modifications are, dominantly, rearrangement of alkyl-aryl ether bond that links the methoxyphenols together to yield methoxyphenols linked by an aryl-alkyl bond between the structural units, as well as some demethylation of methoxy groups yielding catechol-like structures (4). The transformation of coalified wood from lignite through the subbituminous rank range to high volatile C rank bituminous coal is characterized by transformations which result in complete demethylation of methoxyphenols to catechols and a subsequent reduction of the catechol-like structures, presumably through reaction, to form phenol-like structures (6, 8, 9). The focus of this paper is to review our current understanding of the evidence for these aforementioned chemical transformations and to present these reactions within the context of a new three-dimensional helical model that has been developed for lignin (10).

## PEATIFICATION

It was made especially clear from studies of fresh wood and peatified wood (1, 7, 9) that cellulosic components of wood, the ones contributing more than 60% of the structure, essentially are mineralized or degraded and lost within a short span of time geologically. Thus, the cellulosic components do not play a significant role in the structural make-up of coalified wood. The lignin, however, is selectively preserved in a relatively unaltered state during peatification and is the substance which eventually forms the coalified wood's vitrinitic component.

Perhaps the most astounding aspect of this degradative process is the selectivity and structural precision with which it occurs. Essentially all of the major mass component of wood, the cellulose, is lost. One might infer that tremendous physical destruction ensues; however, peatified wood remarkably retains its morphology. This can clearly be seen in SEM photomicrographs of degraded wood in peat (11). Delicate wood structures such as bordered pits and cell wall tracheids appear physically intact even though all the cellulose has been degraded. Apparently, the wood has been degraded by bacteria which use extracellular enzymes to enable destruction of the cellulosic materials. This process apparently does not involve physical maceration.

Framed within the context of the helical model of lignin, the degradation of cellulose affects the three-dimensional extension of the helical chain if one considers the cellulose microfibrils on wood to be hydrogen bonded or even covalently bonded to the cellulose (10, 11). The pitch of the helix under such circumstances can be viewed to at a low angle relative to the axial dimension, depending upon how many hydrogen or covalent bonds are formed with the cellulose. In the middle lamellar region of wood cells, the general depletion of cellulose renders lignin helices with

high angle pitches. In the secondary cell wall, the high amount of cellulose provides many bonding sites, allowing the helix to be extended at a low angle pitch.

The loss of the cellulose backbone allows collapse of the helix to its most condensed configuration. This condensed configuration brings into relatively close proximity some important reaction centers for reactions that have been postulated to occur during coalification (11).

#### COALIFICATION TO BROWN COAL AND LIGNITE

The lignin which survives this initial degradative process relatively unscathed, is eventually altered over the course of geological time as wood in peat is buried in sedimentary systems. We know this from studies of coalified wood in brown coals and lignites (3, 4, 8, 9). By comparing the chemistries of peatified wood, mainly lignin, with brown coal or lignitic woods of the same family (e.g., gymnosperms, angiosperms), we can decipher reactions which might be responsible for observed changes. We certainly can identify the nature of chemical changes which occurred. These are depicted in Figure 1.

Perhaps the most chemically and microbiologically labile bond in lignin is the bond linking the methoxyphenolic aromatic monomers together, the  $\beta$ -O-4 bond. Evidence that this bond is cleaved during coalification was provided by Hatcher (3), from an examination of the NMR spectra of brown coal woods. If we consider that all such bonds in lignin are broken and the fact that approximately 60% of the bonds in lignin are of this type, then we might expect the lignin, or the peatified wood, to be completely macerated because rupture of this bond would release molecular fragments which are likely to be soluble in water. Examination of SEM photomicrographs of brown coal wood in which such bond ruptures have occurred shows that physical disruption of the wood anatomy does not occur to any great extent. Delicate structures such as bordered pits would not physically survive a maceration. Also, the SEM photos do not provide any evidence for dissolution or even partial dissolution of cell walls. This must imply that another reaction maintains the macromolecular integrity of the lignin.

The reaction most likely responsible for maintaining structural integrity must be one which allows connectivity between methoxyphenolic structures in lignin. Thus, we must maintain some bond between the aromatic units. Alkylation following  $\beta$ -O-4 bond rupture is the likely reaction. Botto (12) has shown that such an alkylation is possible when lignin labeled at the  $\beta$  carbon is subjected to artificial coalification in the presence of clays. In essence, the rupture of the  $\beta$ -O-4 bond releases a carbocation, the  $\beta$  carbon on the sidechain, which is a good electrophile and will attack positions on the aromatic ring of adjacent phenolic structures which are susceptible to electrophilic substitution (e.g., the C-5 predominantly). The most likely aromatic ring to be alkylated is the one from which the  $\beta$ -O-4 bond rupture occurred. The rupture of the  $\beta$ -O-4 bond would produce a phenol which would likely activate the C-5 site to alkylation. Evidence that such a reaction occurs in brown coal wood comes from the NMR data which show increased aromatic ring substitution (2, 4). Dipolar dephasing NMR studies indicate that brown coal wood samples have fewer protons per ring than their respective counterparts in peat, indicating that, on the average, one of the ring sites has become covalently bound to an atom other than hydrogen. The NMR data also indicate that the additional substituent atom is not an oxygen but a carbon atom. It is clear that the data all point to the fact that cleavage of the  $\beta$ -O-4 bond during coalification of the lignin in peatified wood leads to an alkylation of an adjacent ring by the resulting carbocation, and this overall process leads to a maintenance of the physical integrity of the wood.

To maintain this integrity observed unambiguously from SEM data it is necessary that the above reaction occur without much structural rearrangement of the lignin. In other words, the reaction must proceed rapidly and must occur at a relatively proximal site to the  $\beta$ -O-4 cleavage. If one considers a lignin model as one which is random in the connectivity between methoxyphenolic units (13, 14), then the likelihood that structural order will be maintained with the above-mentioned transformation is minimal. In a random model, distances between aromatic reaction centers are variable and some significant physical disruptions will ensue if the carbocations formed from  $\beta$ -O-4 bond rupture have to link up with aromatic centers which are more than just local.

The recently proposed ordered model for lignin (10) would overcome this problem. The order is believed to derive from the fact that the methoxyphenolic units linked by the  $\beta$ -O-4 bonds in lignin exist in an helical conformation. With such a configuration, cleavage of this bond releases a carbocation which is in relatively close proximity to the C-5 site on the aromatic ring. The alkylation of this site causes minimum disruption of the helical order as a  $\beta$ -C-5 bond is formed. Thus, we might also expect minimum disruption of the physical integrity of the sample, consistent with what is observed in brown coal wood.

Another important coalification reaction which is observed to occur through the lignite stage of coalification is the cleavage of other aryl-O bonds in lignin. The specific bonds are those of

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methoxyl groups attached to the aromatic ring. Both NMR and py/gc/ms data show that this is happening (2, 9). The chemical degradative data of Ohta and Venkatesan (8) also show this reaction. All these studies indicate that the loss of methoxyl is through a demethylation process whereby the bond between the methyl carbons and the oxygen attached to the ring is cleaved. The molecular modeling studies show that the helical configuration is not affected by such a reaction (11). The resulting structure of the coal contains a phenol where there once was a methoxyl group, and the structure is now said to have one similar to that of catechols, if one considers that the cleavage of the  $\beta$ -O-4 bond has already occurred.

Additional changes in lignin structure are more subtle, but somewhat evident from NMR data. In lignin and peatified wood, the sidechains are hydroxylated at both the  $\alpha$  and  $\gamma$  sites. Loss of hydroxyl groups from the sidechains is another reaction resulting from coalification of the lignin. NMR resonances attributable to these hydroxyls diminish substantially during coalification through to the rank of subbituminous coal. Simple loss of the sidechain units by a pyrolytic process would explain the loss of these resonances, but this would lead to a significant increase in aromaticity. Because aromaticities of coalified wood samples do not increase over the course of the observed loss of hydroxyls, it is likely that simple reduction of the hydroxyls to alkyl groups is the preferred pathway. This would shift the NMR resonances into the alkyl region of the spectra and preserve carbon aromaticities. Such a reaction would also be consistent with the physical structural data, because reduction of hydroxyls would maintain the presumed helical conformation and would cause minimum disruption of the helical macromolecular structure. Pyrolytic loss of the sidechain carbons would likely macerate the structures beyond recognition. Clearly, to preserve physical integrity to the rank of brown coal or even lignite, the side chains must not be lost.

The eventual structural model which can be drafted based on the helical lignin template and altered by the coalification processes mentioned above is shown in Figure 2. It is difficult to display and to describe all the features of such a model in two dimensional space, but one can discern readily that an helical configuration is apparent, even though some significant chemical changes have ensued.

#### COALIFICATION TO SUBBITUMINOUS AND BITUMINOUS COAL

The transformations of brown coal and lignitic woods to higher rank involve some significant changes in chemical structure. This is perhaps the primary cause for the change in physical morphology often observed as coal becomes more lustrous and the vitrinite becomes more homogeneous. This transformation has often been referred to as gelification (15). The wood cells have become deformed significantly, presumably due to increased burial pressure, and some cells actually become annealed to a homogeneous mass.

While structures in brown coal and lignite are dominated by the catechol-like rings arranged in an helical conformation perhaps, the major components of subbituminous and bituminous woods are phenol-like structures. Evidence for the transformation of catechol-like structures to phenol-like structures as shown in Figure 3 comes from both NMR and py/gc/ms data (4, 6). The NMR data clearly indicate a loss of aryl-O carbon. In lignite, aryl-O carbons account for approximately 2 of the six aromatic carbons on the ring, whereas in subbituminous and bituminous coal, only 1 of six aromatic carbons is an aryl-O carbon. Pyrolysis data demonstrate the same observation, with lignitic wood samples being rich in catechols and subbituminous wood samples being rich only in phenols and alkylated phenols. Elemental data show that a significant diminution of oxygen content can explain these transformations.

Coalification to the rank of high-volatile bituminous coal leads to further reductions in oxygen contents for coalified wood. Considering the fact that the amounts of aryl-O do not change significantly, it is likely that the changes imply a further condensation of phenols to aryl ethers or dibenzofuran-like structures as shown in Figure 4 (6). The py/gc/ms data confirm this as more alkylbenzenes and dibenzofurans are observed. The alkylbenzenes in pyrolyzates could arise from thermal cracking of dibenzofuran or diaryl ethers during flash pyrolysis. Also, the increased quantities of condensed aromatic rings, naphthalenes and fluorenes, in pyrolyzates suggests that aromatic ring condensation is occurring. It is likely that this condensation will disrupt the helical structure proposed. At this time we have little to offer in the way of a mechanism for this condensation. Aromaticity of coalified wood appears to increase at this rank (2), suggesting that one possible route for the formation of condensed rings is ring closure and aromatization of the alkyl sidechains. Further studies are needed to verify such a pathway.

Perhaps the next most apparent difference between woods coalified to the rank of subbituminous / bituminous coal and those at the rank of lignite or lower rank is the lack of oxygenated alkyl structures (i.e., hydroxyls or alkyl ethers). The NMR data for subbituminous and bituminous coalified woods show essentially baseline in this region of the spectra, evidence that such functional groups are not significant. Thus what were originally hydroxylated lignin sidechains have been altered. As discussed above, it is most likely that the lignin-derived hydroxyl groups have been reduced rather than lost by pyrolysis of the sidechain. The reduction of hydroxyls is essentially complete at the rank of subbituminous coal.

Consequently, the structural composition of subbituminous coal is that of a lignin structure which has lost its methoxyl groups (via demethylation and dehydroxylation) and all its hydroxyls and alkyl ethers. Presumably, all these reactions can occur with minimal disruption of the three dimensional helical network inherited from lignin. Indeed, some semblance of cellular morphology still remains at the rank of subbituminous coal (11). Pressure and temperature begin to combine at these and higher ranks to have a significant effect on physical morphology of wood. Thus, it becomes less clear whether loss of morphology is purely a physical or chemical phenomenon or both. With such a disruption in the macromolecular structure of wood brought on by the formation of condensed ring systems, it seems reasonable that cellular morphology which persists well up to the rank of bituminous coal begins to degrade into a homogeneous glassy appearance with little semblance of cell wall boundaries at ranks of bituminous coal or higher.

The helical structure is less apparent for wood coalified to bituminous coal (Figure 5) because some significant disruptions of the helix are induced by the reactions at this rank level. Condensations of phenols to diaryl ethers and dibenzofurans are primarily responsible for these disruptions of the helix which are likely to be manifested by physical disruptions in the coalified wood.

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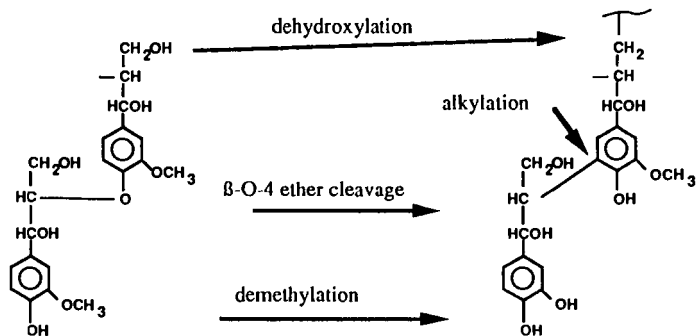


Figure 1. Reactions responsible for the transformation of lignin in peatified gymnospermous wood to brown coal and lignitic wood.

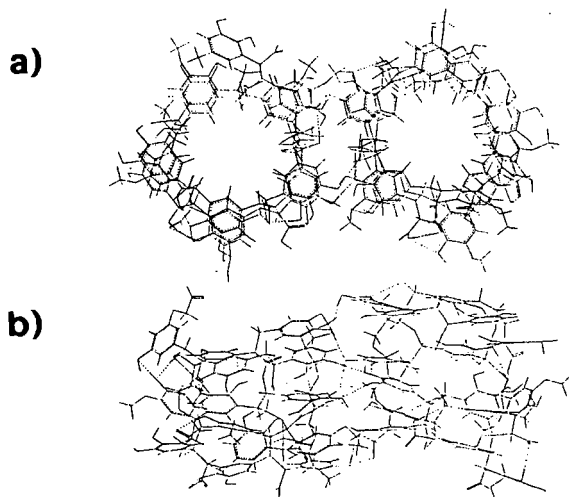


Figure 2. Two dimensional projections of the three dimensional helical model for brown coal and lignitic gymnospermous wood. a) Plan view of the structure and b) elevation view.

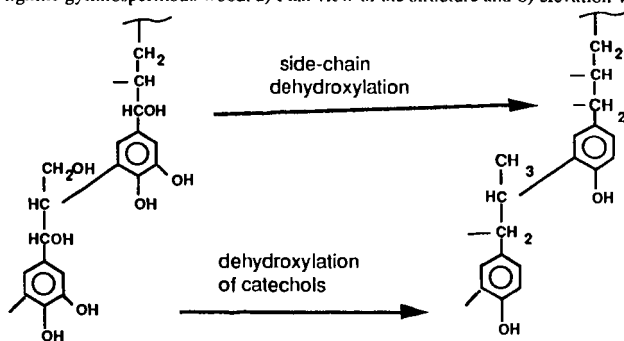


Figure 3. Reactions proposed for the transformation of lignitic gymnospermous wood to subbituminous coal wood.

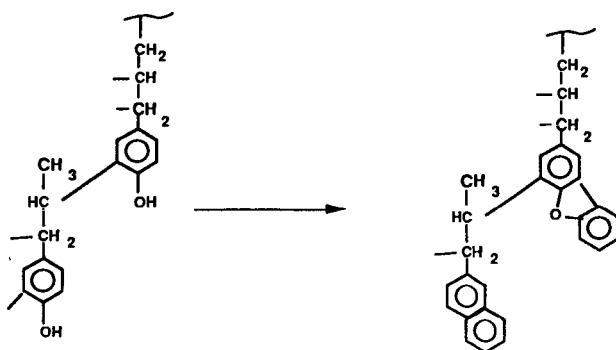


Figure 4. Reactions proposed for the transformation of subbituminous wood to bituminous wood.

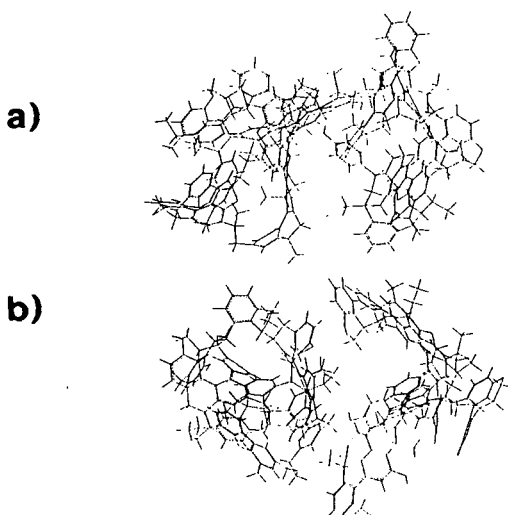


Figure 5. Structural model for bituminous coalified wood built from the helical lignin template and showing a) plan and b) elevation views of the three dimensional structure which has been energy minimized by methods outlined in Faulon and Hatcher ().